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Silicalite samples with Si/Al ratios of 126, 563, and 1062 were characterized in terms of adsorption and diffusion with water, methanol, benzene and n-hexane at 25°C. The Characterization was carried out by the gravimetric method with a Cahn electro-balance in a constant-volume and constant-temperature system. It was found that (1) the saturation equilibrium adsorption capacity for water in silicalite decreases as the Si/Al ratio increases; (2) the effect of Si/Al ratio on the saturation equilibrium adsorption capacity of organics in silicalite is small; and (3) the diffusion of guest molecules in silicalite depends primarily on the size of the guest molecules. Additionally, a comparison of hydrophobic properties of silicalite and activated carbon was made. The result indicates that the water adsorption capacity of silicalite is about twelve times less than that of activated carbon. Hydrophobicity of silicalite increases substantially after fluorination (F-silicalite).

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CHARACTERIZATION OF HYDROPHOBIC NATURE OF HIGH SILICEOUS  
ZEOLITE-SILICALITE BY ADSORPTION AND DIFFUSION

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ABSTRACT

Silicalite samples with Si/Al ratios of 126, 563, and 1062 were characterized in terms of adsorption and diffusion with water, methanol, benzene and n-hexane at 25°C. The characterization was carried out by the gravimetric method with a Cahn electro-balance in a constant-volume and constant-temperature system. It was found that (1) the saturation equilibrium adsorption capacity for water in silicalite decreases as the Si/Al ratio increases; (2) the effect of Si/Al ratio on the saturation equilibrium adsorption capacity of organics in silicalite is small; and (3) the diffusion of guest molecules in silicalite depends primarily on the size of the guest molecules. Additionally, a comparison of hydrophobic properties of silicalite and activated carbon was made. The result indicates that the water adsorption capacity of silicalite is about twelve

times less than that of activated carbon. Hydrophobicity of silicalite increases substantially after fluorination (F-silicalite).

## INTRODUCTION

Zeolite with high Si/Al ratio (ZSM-5, silicalite, dealuminated mordenite) have long recognized to possess hydrophobic properties [1-3]. The degree of hydrophobicity is normally dependent on the Si/Al ratio. Olson et al [2] and Nakamoto [3] showed that the amount of water adsorbed decreased linearly with an increase in Si/Al ratio. In this study, the uptake data of water, methanol, benzene, and n-hexane on silicalite with three different Si/Al ratios were obtained at 25°C. The primary objective of the study is to investigate the hydrophobic property of silicalite by studying the effects of Si/Al ratio on the equilibrium adsorption capacity and diffusion coefficient of water and hydrocarbons.

## EXPERIMENTAL

Material. The silicalite samples were provided by Union Carbide with the Si/Al ratios of 126, sample A (Lot 9959-58); 563, sample B (Lot 8496-79); 1058, sample C (Lot 8497-30-1); and a proprietary F-silicalite sample (Lot 11689-60). The physical properties of these samples are summarized in Table 1. It should be noted that the BET surface area is not a significant way for the characterization of adsorptive property of zeolite due to its unique crystalline structure.

Adsorption Measurement. Both adsorption and diffusion measurements were carried out by the gravimetric method with a Cahn RG electro-balance in a constant-volume and constant-pressure system similar to that of Ma and Wu [4]. A schematic diagram of the system is shown in Figure 1. The entire unit was housed in an insulated cabinet to maintain a constant temperature. The silicalite sample was activated under  $10^{-4}$  torr and  $350^{\circ}\text{C}$  until no

Table 1. Physical Properties of the Silicalite Samples

<u>Sample</u>	<u>Si/Al Ratio</u>	<u>BET Surface Area, <math>\text{m}^2/\text{g}</math></u>	<u>Mean Particle Size, <math>\mu\text{m}</math></u>
A	126	400	3.5
B	563	438	2.1
C	1062	437	2.1

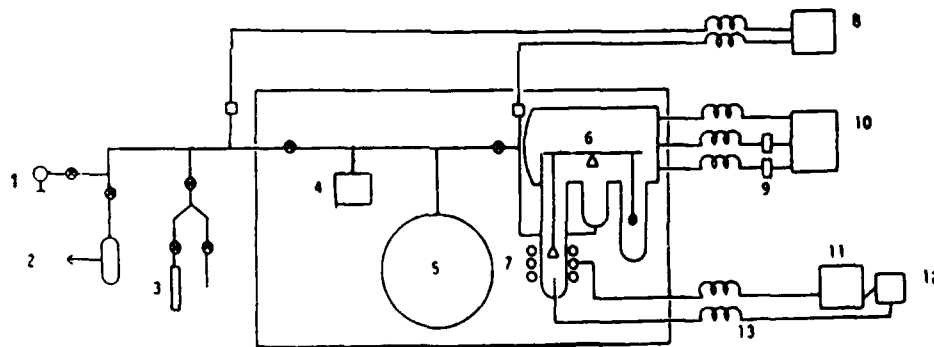


Figure 1. Apparatus. 1. MKS Pressure Gauge; 2. Vacuum Pump; 3. Liquid Reservoir; 4. Baratron; 5. Gas Reservoir; 6. Balance Assembly; 7. Split Tube Furnace; 8. Thermal Conductivity Vacuum Gauge; 9. Electronic Ice Points; 10. 3-Channel Temperature and Mass Recorder; 11. Autotransformer; 12. Temperature Controller; 13. Type J Thermocouple Wires.

weight change was observed. The sample was then isolated by means of a stopcock. The reservoir was filled with vapor to the desired pressure which was measured by an MKS Baratron calibrated from 0.001 to 1000 mm Hg

in conjunction with the reference side standard pressure arrangement. At the start of a run, the stopcock isolating the balance was opened and the adsorbate was admitted into the assembly. The change in adsorbent weight as a function of time was continuously recorded until equilibrium was achieved. Unique to the current gravimetric system was the fact that the system pressure, the sample temperature and the sample weight change could be monitored simultaneously during the entire sorption process. This unique feature allowed us to control the temperature rise during sorption to be less than 1-2 K by using small pressure steps. This made the thermal effect on sorption small and negligible.

#### RESULTS AND DISCUSSION

The equilibrium adsorption isotherms of water for silicalites of three Si/Al ratios at 25°C are shown in Figure 2. For the purpose of comparison, the equilibrium adsorption isotherms of water, n-hexane, benzene, and methanol at 25°C are shown in Figure 3 with amount adsorbed expressed as relative pressure (ratio of pressure and the adsorbate's vapor pressure at 25°C). The equilibrium saturation capacities for all adsorbates are summarized in Table 2 long with values reported by Flanagan et al [5]. It is evident from Figure 2 and Table 2 that the equilibrium saturation capacity of water decreases substantially with an increase in Si/Al ratio exhibiting the remarkable hydrophobic nature of the high siliceous zeolite. This hydrophobic property is even more pronounced when the Si/Al ratio is greater than 500. The low water adsorption saturation capacity of around

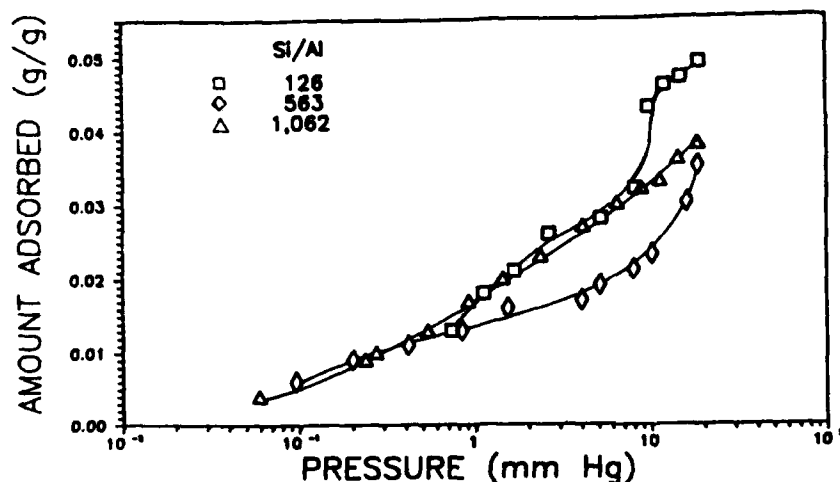


Figure 2. Adsorption Isotherm for Water in Silicalites.

3.7 wt% is considerably lower than that generally exhibited by zeolites (~15-25%).

The effect of the removal of aluminum from the zeolite on the equilibrium adsorption capacities of hydrocarbons appears to be small. Furthermore, they are considerably higher than those of water and appear to increase slightly with an increase in Si/Al ratio as shown in Figure 3. In fact, the adsorption capacities of these organics appear to be consistent with pore filling process. For example, if one assumes the density of the adsorbate in silicalite to be the same as that of the normal liquid, the computed liquid volume of n-hexane adsorbed on the silicalite is around 0.2 cm<sup>3</sup>/g which is approximately equal to the silicalite pore volume of 0.19 cm<sup>3</sup>/g. As silicalite is hydrophobic, one would expect the adsorbed volume of methanol to be less than that of water as shown in Table 2. The adsorbed volume for benzene is considerably smaller than the pore volume of silicalite. This is to be expected as benzene molecules are rather rigid and can not be effectively packed in the pores [6].

The fact that the equilibrium adsorption capacities for the organics are relative insensitive to the Si/Al ratio as shown in Table 2 makes it possible to use silicalite for the removal of organics in the presence of

Table 2. Saturation Adsorption Capacities of Hydrocarbon and Water in Silicalite at 25°C

Adsorbate	Kinetic Diameter, A	Adsorption Capacity (g adsorbed/g adsorbent)				Liquid Density of Adsorbate, 25°C
		A	B	C	Silicalite <sup>1</sup>	
Water	2.65	.050 (.050)	.035 (.035)	.038 (.038)	.047 (.047)	.998
n-Hexane	4.30	.115 (.174)*	.129 (.197)	.132 (.200)	.131 (.199)	.659
Methanol	3.80	.097 (.122)	.130 (.164)	.120 (.152)	.153 (.193)	.791
Benzene	5.85	.098 (.111)	.103 (.116)	.101 (.114)	.119 (.134)	.885

<sup>1</sup>Reference 5.

\*Value in Parenthesis is the Saturation Adsorption capacity Computed Based on Liquid Density (cm<sup>3</sup>/g).

water molecules. One proposed scheme for such application is to use silicalite for the removal of ethanol in dilute aqueous solutions. Similar application can be carried out in the vapor phase. The low water adsorption capacity in conjunction with a substantial adsorption capacity for organics makes silicalite an ideal adsorbent for the removal of contaminants in the presence of water. However, the effectiveness of adsorbing other gases in the presence of water would have to be tested by performing mixture adsorption experiments.

The diffusion coefficients for the adsorbates studied are in the order

of  $10^{-9}$  cm<sup>2</sup>/s. The data showed that diffusion coefficients decrease in the following order:  $D_{\text{water}} > D_{\text{methanol}} > D_{\text{n-hexane}} > D_{\text{benzene}}$ . This appears to show that the size of the diffusing molecule plays a relatively important role in the movement of the molecules inside the silicalite channels. The calculated diffusion coefficients at low coverages are summarized in Table 3. It appears that the diffusion coefficients decrease as the Si/Al ratio increases. The reason for such a decrease on diffusion coefficients is unclear. However, it is possible that this is caused by the blockage of the channels due to the existence of extra-silanol groups recently reported to be existing in high siliceous ZSM-5 [7-8].

Table 3. Diffusion Coefficients at Low Coverage

Adsorbate	Diffusion Coefficients x $10^9$ cm <sup>2</sup> /s		
	A	B	C
n-Hexane	7.75	2.68	2.03
Benzene	5.85	2.80	2.03
Methanol	14.53	11.70	3.99
Water	16.71	14.14	7.96

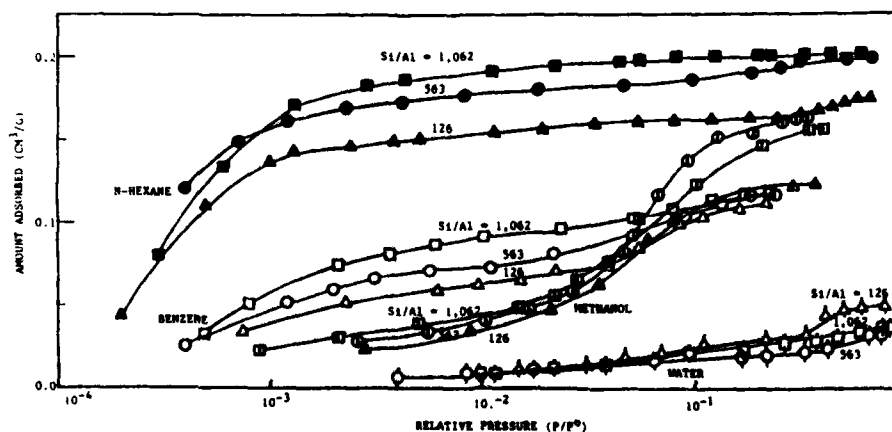


Figure 3. Adsorption Isotherms of Silicalite at 25°C.

Similar adsorption isotherms were measured using fluorinated silicalite (F-silicalite). The water adsorption capacity of F-silicalite reduces about four times than that of silicalite while the organics adsorption capacity decrease about only 2%, Figure 4 and Table 4. In the decreasing adsorption capacity of organics for F-silicalite, the order would be n-hexane, methanol, and benzene comparable to that of silicalite shown in Figure 3. A comparison of hydrophobic properties of silicalite and activated

Table 4. Saturation Equilibrium Adsorption Capacities of Water and Hydrocarbons on F-Silicalite\* at 25°C.

Adsorbate	Kinetic Diameter, A	Adsorption Capacity			Adsorbate Liquid Density, g/cm <sup>3</sup>	P <sup>0</sup> (mm Hg) at 25°C
		(mg/g)	(mmole/g)	(cm <sup>3</sup> /g)		
Water	2.65	9.47	0.53	0.010	0.998	23.8
n-Hexane	4.30	99.20	1.15	0.151	0.659	148.4
Methanol	3.80	91.82	2.87	0.116	0.791	85.6
Benzene B	5.85	84.40	1.08	0.095	0.885	115.6

\*F-Silicalite samples from Union Carbide (Lot # 11689-60).

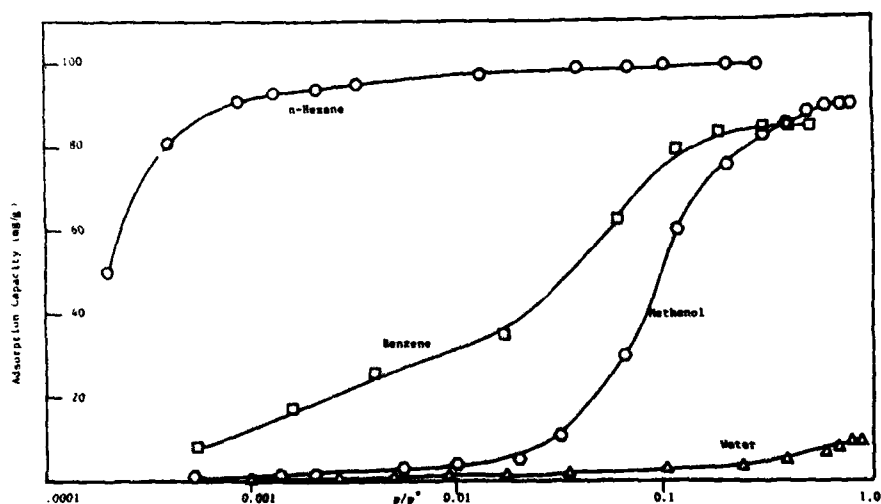


Figure 4. Equilibrium Adsorption Isotherms of F-Silicalite.

carbon [10] was made. The result indicates that the water adsorption capacity of silicalite is about twelve times less than that of activated carbon with comparable adsorption capacity of organics for both adsorbents except benzene at 25°C as shown in Table 5. Fluorination of silicalite further increases its hydrophobicity to forty six times less than that of activated carbon with slightly decrease in organics adsorption for fluorinated silicalite (F-silicalite), Table 6. It appears that fluorination does not block up the pores in silicalite for adsorption and that fluorinated silicalite provides superior hydrophobicity characteristics. Such highly hydrophobic property deems desirable for application in the hot and humid environment.

Table 5. Comparison of Saturation Adsorption Capacity of Activated Carbon and Silicalite at 25°C

<u>Adsorbate</u>	<u>Activated Carbon</u>	<u>Silicalite<sup>1</sup></u>	<u>Act. Carbon/Silicalite</u>
Water	43.65%	3.8%	11.5
Benzene	40.94%	10.1%	4.1
Methanol	17.60%	12.0%	1.5
n-Hexane	22.25%	13.2%	1.7

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<sup>1</sup>Si/Al Ratio of Silicalite is 1062.

Table 6. Comparison of Saturation Adsorption Capacity of Activated Carbon and F-Silicalite at 25°C

<u>Adsorbate</u>	<u>Activated Carbon</u>	<u>F-Silicalite<sup>2</sup></u>	<u>Act. Carbon/F-Silicalite</u>
Water	43.65%	0.95%	46.0
Benzene	40.94%	8.40%	4.9
Methanol	17.60%	9.20%	1.9
n-Hexane	22.25%	9.92%	2.2

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<sup>2</sup>Si/Al Ratio of F-Silicalite is greater than 200.

## CONCLUSIONS

The conclusions from the present investigation are listed as follows:

1. The saturation equilibrium adsorption capacity for water in silicalite decreases as the Si/Al ratio increases.
2. The effect of Si/Al ratio on the saturation equilibrium adsorption capacity of organics in silicalite is small.
3. The diffusion of guest molecules in silicalite depends primarily on the size of the guest molecules.
4. Both silicalite and F-silicalite exhibit higher hydrophobicity than activated carbon with comparable adsorption capacity for organics except benzene.
5. F-silicalite has four times higher hydrophobicity than that of silicalite.

## REFERENCES

- [1] Chen, N. Y., Phys. Chem., 80, 60 (1976).
- [2] Olson, D. H., Haag, W. O., and Lago, R. M., J. Catal., 61, 390 (1980).
- [3] Nakamoto, H. and Takahashi, H., Zeolites, 2, 67 (1982).
- [4] Wu, P. and Ma, Y. H., in "Proceedings of the Sixth International Conference on Zeolites," ed., D. Olson and A. Bisio, Butterworth, p. 251 (1984).
- [5] Flanagan, E. M., Bennett, J. M., Grose, R. W., Cohen, J. P., Patton, R. L., Kirchner, R. M., Smith, J. V., Nature, 271, 512 (1978).
- [6] Wu, P., Debebe, A., and Ma, Y. H., Zeolites, 3, 118 (1983).

- [7] Chester, A. W., Chu, F. Y., Dessau, R. M., Kerr, G. T., Kresge, C. T., J. Chem. Soc. Chem. Commun., 289 (1985).
- [8] Woolery, G. L., Alemany, L. B., Dessau, R. M., and Chester, A. W., Zeolites, 6, 14 (1986).
- [9] Derouane, E. G., Hubert, R. A., Chem. Phys. Letters, 132, 315 (1986).
- [10] Noyes, Jr. W. A., Summary Technical Report of the National Defense Research Committee, Division 10, 142 (1946).